

Kinetics: Differential and Integrated Rate Laws

PURPOSE

- Observe and compare the effects of homogeneous and heterogeneous catalysts on the decomposition of hydrogen peroxide
- Measure reaction rates to determine the order of reaction with respect to various reactants
- Analyze experimental data to write a differential rate law expression
- Analyze decay data to determine the integrated rate law constant for a radioactive substance

INTRODUCTION

The study of the rates of chemical reactions is called **kinetics**. Reactions are altered by a number of factors that may be exploited to control their rates. A kineticist will study these factors for a given reaction, considering them as a means to control the rate of the reaction so that it might be studied thoroughly in the laboratory or, possibly, monitored for effectiveness as an industrial process.

On a molecular basis, the collision theory of chemical reactions predicts that reacting particles must collide in a particular way to allow a reaction to occur. The collision will be an effective one only if the reacting particles collide with sufficient kinetic energy to allow rupture of any existing bond. Further, the reacting particles must strike each other in an orientation that allows a new chemical bond to form. Only if both of these criteria are met will an effective collision occur and a chemical reaction ensue. The vast majority of these collisions between potentially reacting particles are ineffective and do not lead to a chemical reaction. A step-by-step description of the process on a molecular level is called a **reaction mechanism**.

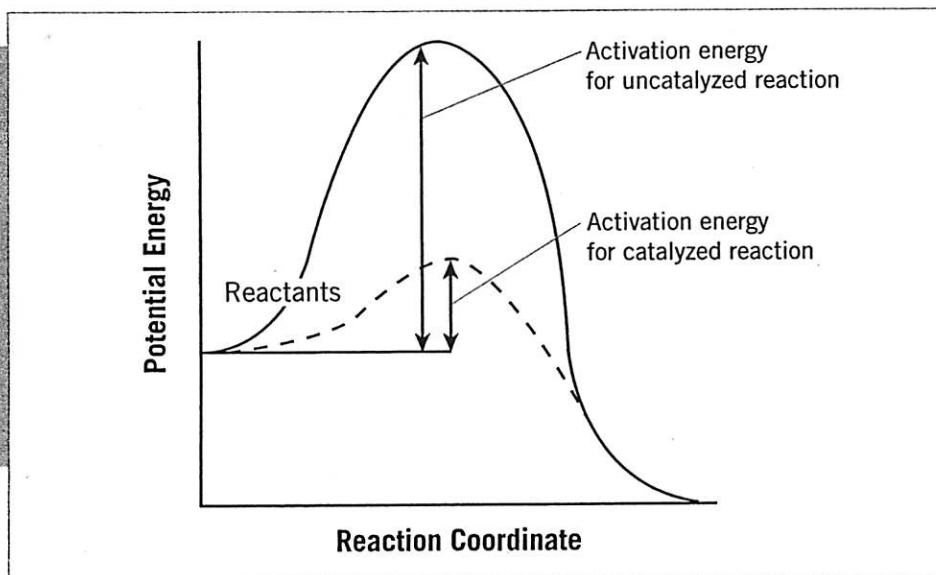
There are a number of factors that alter reaction rate. These include:

- concentration
- temperature
- chemical characteristics
- surface area of reactants
- presence of a catalyst

Each of these characteristics may alter the rate of reaction. Increasing the *concentration* of a substance means that more particles are available to collide, potentially leading to more effective collisions. Increasing the *temperature* of a system should cause a greater fraction of reacting particles to carry enough kinetic energy to break existing bonds. Some reactants are more likely to react quickly because of *chemical characteristics*; for example, the metal magnesium is more reactive than the metal iron. Although a piece of magnesium will burst into spectacularly bright flame if introduced to a Bunsen burner flame, a similar piece of iron will merely glow red if placed in the same flame. To cause a reaction as dramatic as that of magnesium, the red-hot iron might be dropped into a container of pure oxygen. Or, the *surface area* of the iron—another factor affecting reaction rate—might be increased greatly. As an example of this factor, a piece of steel wool burns much more readily than does the same mass of iron in the form of a solid piece.

Finally, the rate of a chemical reaction may be altered by a **catalyst**, a substance that is not itself consumed in the reaction. Most catalysts cause an increase in the rate of reaction. Some cause the opposite effect and slow the chemical reaction. These negative catalysts are called **inhibitors**. In general, catalysts fall into two groups, depending on phase: **homogeneous** catalysts are found in the same phase as the reacting substances, whereas **heterogeneous** catalysts are in a different phase.

Figure 13.1
A catalyst alters the pathway of a chemical reaction so that the alternate path has a lower activation energy, and more rapid reaction rate, than the uncatalyzed reaction.



Because the rate of a chemical reaction is influenced by the concentration of the reactants, a rate law can be developed to quantify the relationship. The rate law follows the general form

$$\text{Rate} = k [\text{reactant A}]^x [\text{reactant B}]^y$$

where x and y are the orders of the reactants. A reactant is said to be **first order** if a change in its concentration causes a direct corresponding change in the rate of reaction; hence doubling the concentration would cause a doubling of the reaction rate. A **second order** reactant causes an exponential change; hence, doubling the concentration of a second order reactant will cause a 2^2 , or four-fold, increase in the reaction rate. Changing the concentration of a **zero order** reactant causes no change in the reaction rate. The order of a reaction must be determined experimentally and cannot be gleaned from the coefficients of a balanced chemical equation.

Procedure Preview In this lab, you will develop kinetics data for two kinds of rate laws. First, data for **differential rate law** will be determined experimentally by altering the concentrations of reactants in a predictable fashion, then measuring the changes in *initial rates* that occur as a result of the changes in concentration. Thus multiple trials are required. The behavior of each trial is compared to that of the other trials as you calculate the order of each reactant in the equation.

Data for **integrated rate law** are to be determined in a different way. Only a single trial is required and the concentration of a reactant is measured at different times. The results of those measurements are then plotted in several ways to determine the order of a reactant. A first-order reactant A will give a straight line if the natural log of the concentration of A is plotted versus time:

$$\ln[A]_t - \ln[A]_o = -kt \text{ or}$$

$$kt = \ln\left(\frac{[A]_o}{[A]_t}\right)$$

Note that the slope of the line is equal to the opposite of k .

A second-order reactant A will give a straight line if inverse concentration of A is plotted versus time:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Note that the slope of this line is equal to k .

A zero-order reactant A will give a straight line if $[A]$ versus time is plotted and the slope of the line is equal to the opposite of k .

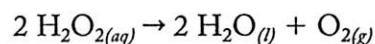
Table 13.1
Summary of kinetics for reaction of reactant R until time t (or $R_0 \rightarrow R_t$)

Characteristic	If Zero Order	If First Order	If Second Order
Differential rate law	Rate = $k[R]^0$	Rate = $k[R]^1$	Rate = $k[R]^2$
Integrated rate law	$[R]_t = -kt + [R]_0$	$\ln[R]_t = -kt + \ln[R]_0$	$\frac{1}{[R]} = kt + \frac{1}{[R]_0}$
Straight line graph	$[R]$ vs t	$\ln[R]$ vs t	$\frac{1}{[R]}$ vs t
k and slope m of line	$m = -k$	$m = -k$	$m = k$
Half-life $t_{1/2}$	$t_{1/2} = \frac{[R]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[R]_0}$

PART A: Differential Rate Law: Catalyzed Decomposition of H_2O_2

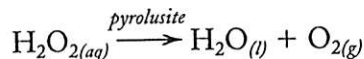
In this part of the lab, you will study the effects of different kinds of catalysts on the decomposition of hydrogen peroxide by employing two different methods. In the first method, the mineral pyrolusite will provide a convenient surface for the decomposition of the hydrogen peroxide. This mineral is a heterogeneous catalyst, and its pitted surface provides an attractive site for the reaction to occur. In the second method, a homogeneous catalyst, a solution of potassium iodide, will be used. In this case, the iodide in the KI is actually involved in the chemistry of the reaction. However, because the KI is regenerated and found in the same form in which it originally existed, it meets the criteria to be considered a catalyst.

Hydrogen peroxide is unstable and **disproportionates** easily to form water and oxygen gas over time. Disproportionation changes a substance, with oxidation and reduction occurring concurrently. In this reaction, oxygen changes from an oxidation number of -1 in the peroxide ion to a zero oxidation number, as the elemental form of oxygen gas, and to a -2 oxidation number, as oxygen combined with hydrogen in the water molecule.



This reaction is slow, but it is commonly catalyzed using manganese(IV) oxide. Using a simple apparatus, the rate of the decomposition can be monitored on the small scale by counting the number of oxygen bubbles formed during a certain time period. This count will serve as a measure of the rate of formation of oxygen. It is assumed that the pressure inside the reaction flask builds to a constant level. After that pressure is reached, the number of bubbles produced in the water at the small tip within the reservoir is a direct result of additional oxygen generated in the flask by the decomposition of the hydrogen peroxide.

Method 1: Heterogeneous Catalyst



You will perform this experiment using five solutions of H_2O_2 (10% initially, then diluted to 5%, to 3.3%, to 2.5%, and to 1%). You will then graph log rate (bubbles per second) versus log concentration (% H_2O_2) to obtain the reaction order with respect to H_2O_2 .

Because this is a decomposition reaction and the catalyst does not appear in the rate law,

$$\text{rate} = k[\text{H}_2\text{O}_2]^x$$

Taking the log of both sides of the equation yields

$$\log \text{rate} = \log k + x \log [\text{H}_2\text{O}_2]$$

$$\log \text{rate} = x \log [\text{H}_2\text{O}_2] + \log k$$

If you graph this relationship, note that the plot will take the familiar form of a linear equation

$$y = mx + b$$

where $y = \log \text{rate}$, $x = \log [\text{H}_2\text{O}_2]$, the y -intercept $b = \log k$, and $m = x$, the order of the H_2O_2 . For this reason, determining the slope of the line that you plot will allow you to determine the order of the hydrogen peroxide in this decomposition reaction.

MATERIALS

- 50-mL Erlenmeyer flask
- one-hole rubber stopper attachment, containing Beral pipet bulb and micropipet tip insert (see Appendix E on page 144)
- pyrolusite
- 10% H_2O_2 solution (diluted to 5%, 3.3%, 2.5% and 1.0% solutions)
- microstir bar (see Appendix C on page 140)
- magnetic stir plate
- 10-mL graduated cylinder
- distilled water

PROCEDURE

Step A Ready the following materials:

- 50-mL Erlenmeyer flask
- piece of pyrolusite approximately the size of a finger tip
- reservoir apparatus made from a Beral pipet bulb, micropipet tip and one-hole rubber stopper

Step B Use forceps to place the piece of pyrolusite and the magnetic stir bar in the flask, and place flask on magnetic stirrer so stir bar will not hit the piece of pyrolusite. (Do not touch the pyrolusite with your fingers because the oils from your skin will adversely affect the catalyst.) Turn on the magnetic stir plate to test the placement of the stir bar and the catalyst. Reposition if needed.

Step C Dilute 10% hydrogen peroxide to make 10.0 mL of the appropriate H_2O_2 solution in a graduated cylinder. The 5% solution will require 5 mL 10% solution and 5 mL distilled water, and so on.

Step D Add this solution to the flask and quickly place the reservoir apparatus securely on top of the flask. Quickly fill the bulb more than $\frac{1}{2}$ full with distilled water and insert securely into the mouth of the Erlenmeyer flask. Swirl the flask to mix the solution and wash it across the pyrolusite. Wait 30–45 seconds, until bubbles begin to appear regularly. Then count the number of oxygen bubbles released during a two-minute period. (*Hint:* for an accurate count of bubbles released, record each bubble by keeping a running tally on paper.)

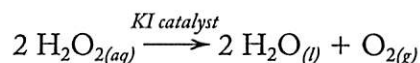
Step E Repeat with the other concentrations of hydrogen peroxide.

Calculations (Method 1)

1. Present all your data in tabular form.
2. Represent your total number of bubbles counted as a rate of bubbles/minute.
3. On graphing paper, plot your results to determine the reaction order with respect to H_2O_2 . Perform a regression line analysis on the points. The slope of this line will be the order of the reaction with respect to the hydrogen peroxide.

Method 2: Homogeneous Catalyst

For the reaction



the rate depends both on the $[\text{H}_2\text{O}_2]$ and $[\text{KI}]$. You will measure the rate of formation of O_2 gas by counting the number of O_2 gas bubbles that are released during a 3-minute period. You will vary the concentrations of H_2O_2 and KI in a systematic way to determine the reaction order with respect to each.

MATERIALS

- 50-mL Erlenmeyer flask
- one-hole rubber stopper attachment (containing Beral pipet bulb and micropipet tip insert)
- 10% H_2O_2
- 0.1 M KI
- distilled water
- microstir bar
- magnetic stir plate
- 10-mL graduated cylinder

PROCEDURE

- Step A** Use the same apparatus with a magnetic stir bar as in Method 1, but without pyrolusite. Add the appropriate volumes of H_2O and 0.1 M KI to the flask, as outlined in Table 13.2, then add the H_2O_2 .
- Step B** Place the bubbling lid securely on top of the flask, quickly fill it 2/3 up with distilled water, and cover. Begin swirling flask to mix, and wait about 30–45 seconds.
- Step C** Begin counting the number of oxygen bubbles that are released during a three-minute period. (*Hint:* to help keep count of bubbles released, run a tally on a piece of paper.)
- Step D** Repeat for all ratios of reactants outlined in Table 13.2.

Table 13.2 Dilution Scheme for Reactants

Trial	Volume 10 % H_2O_2 (mL)	Volume H_2O (mL)	Volume KI (mL)
1	2.0	14.0	4.0
2	4.0	12.0	4.0
3	2.0	10.0	8.0

Because the total volume is 20.0 mL in each case, the concentrations of each are proportional to the volumes added.

Calculations (Method 2)

1. Present all your data in tabular form.
2. Represent your total number of bubbles counted as a rate of bubbles/minute.
3. Write a generic rate law expression and determine algebraically the reaction order, with respect both to H_2O_2 and KI, using relative rates.

Post-Lab Questions

1. Why is it important to stir the solution in each reaction? Explain what would happen to your experimental results if you did not stir the solution in each case.
2. Do the two catalysts, pyrolusite and KI, work in the same manner to increase the rate of decomposition? Use evidence from your experimental results to prove your response.
3. What would happen to the rate of bubble formation in Method 1 if the pyrolusite were ground into a powder rather than in chunk form?